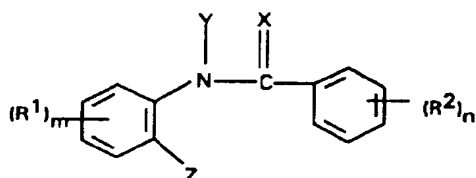




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB96/02279  <b>(22) International Filing Date:</b> 16 September 1996 (16.09.96)  <b>(30) Priority Data:</b> 9518993.2                      16 September 1995 (16.09.95)      GB  <b>(71) Applicant (for all designated States except US):</b> AGREVO UK LIMITED [GB/GB]; Hauxton, Cambridge CB2 5HU (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MOLONEY, Brian, Anthony [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB). RIORDAN, Peter, Dominic [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB). WEST, Peter, John [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB).  <b>(74) Agent:</b> WALDMAN, Ralph, David; AgrEvo UK Limited, Patent Dept., Chesterford Park, Saffron Walden, Essex CB10 1XL (GB).		<b>(81) Designated States:</b> AU, BG, BR, CA, CN, CZ, HU, IL, JP, KR, KZ, MX, NO, NZ, PL, RO, RU, SD, SK, UA, US, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** SUBSTITUTED BENZOIC OR THIOBENZOIC ACID ANILIDES AS FUNGICIDES



**(I)**

**(57) Abstract**

Compounds of formula (I) where: each  $R^1$  and each  $R^2$  is an optionally substituted alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl or amino group, the group  $Y-X$ -, halogen, cyano, nitro, acyl, heterocyclyl, heterocyclyloxy, aryl or aryloxy; or two adjacent groups together with the carbon atoms to which they are attached form an optionally substituted ring;  $Y$  is hydrogen, acyl, or an optionally substituted alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl group;  $Z$  is an optionally substituted 5-membered heterocyclic group comprising 2 or 3 ring heteroatoms selected from nitrogen, oxygen and sulfur, the group being attached to the phenyl through a carbon atom;  $X$  is O or S;  $m$  is 0 to 4; and  $n$  is 0 to 5, are useful as fungicides.

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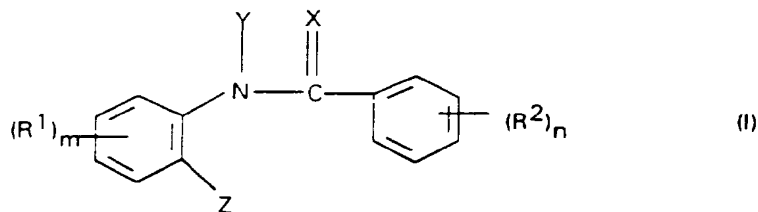
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# SUBSTITUTED BENZOIC OR THIOBENZOIC ACID ANILIDES AS FUNGICIDES

- 5 In our WO 95/25723, there are disclosed fungicidal heterocyclic carboxanilides, carrying a heterocyclic substituent in the 2'-position. We have found that related benzanilides also have valuable fungicidal activity.

In one aspect, the invention provides the use as fungicides of the compounds of  
10 formula I:



where:

- each  $R^1$  and each  $R^2$  is an optionally substituted alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl or amino group, the group Y-X-, halogen, cyano, nitro, acyl,  
15 heterocyclyl, heterocyclyloxy, aryl or aryloxy; or two adjacent groups together with the carbon atoms to which they are attached form an optionally substituted ring;

Y is hydrogen, acyl, or an optionally substituted alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl group;

- 20 Z is an optionally substituted 5 membered heterocyclic group comprising 2 or 3 ring heteroatoms selected from nitrogen, oxygen and sulfur, the group being attached to the phenyl through a carbon atom;

X is O or S;

m is 0 to 4; and

- 25 n is 0 to 5.

Any alkyl group present in the molecule is preferably of 1 to 20, e.g. 1 to 6, carbon atoms. Any alkenyl or alkynyl group is preferably of 3 to 6 carbon atoms. Any cycloalkyl or cycloalkenyl group is preferably of 3 to 8 carbon atoms.

Possible substituents on any alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl group include halogen, cyano, alkoxy (e.g. of 1 to 4 carbon atoms, and which may be substituted, e.g. by halo), hydroxy, alkylthio, nitro, optionally substituted amino, carboxy, alkoxycarbonyl, acyl, acyloxy, heterocyclyl and aryl.

5

Cycloalkyl or cycloalkenyl groups may also be substituted by alkyl.

Aryl groups are usually phenyl, optionally substituted, e.g. by one or more of the same groups as defined for R<sup>1</sup>.

10

The term heterocyclyl includes both aromatic and non-aromatic heterocyclyl groups. Heterocyclyl groups are generally 5 or 6-membered rings containing up to 5 heteroatoms from nitrogen, oxygen and sulfur. The heterocyclyl groups may be fused to a benzene ring to form a fused heterocyclyl group. Examples of heterocyclyl groups are thienyl, furyl, pyridyl, pyrimidinyl, pyrazolyl, thiazolyl, thiazolinyl, oxazolyl, benzimidazolyl, tetrazolyl, benzoxazolyl, thiadiazolyl, oxadiazolyl, dioxolanyl, imidazopyridinyl, 1,3-benzoxazinyl, 1,3-benzothiazinyl, oxazolopyridinyl, triazolyl, triazinyl, imidazolyl, morpholino, benzofuranyl, pyrazolinyl, quinolinyl, quinazolinyl, sulfolanyl, dihydroquinazolinyl, benzothiazolyl, piperidinyl, phthalimido, 2-oxopyrrolidino, 2-oxobenzoxazolin-3-yl and benzofuranyl. Heterocyclyl groups may themselves be substituted, e.g. by one or more groups as defined above for R<sup>1</sup>.

15

20

Z may be one of the 5 membered heterocyclic groups described above but is preferably one where there are hetero atoms in both positions in the ring adjacent the carbon atom by which Z is attached to the phenyl ring. Preferred groups are oxadiazole, thiadiazole, oxazole, oxazoline, thiazole or thiazoline, each of which are optionally substituted by alkyl, especially methyl, haloalkyl, especially dichloromethyl, alkoxy, preferably methoxy, alkylthio, preferably methylthio, cyclopropyl or phenyl, optionally substituted, preferably by halo or alkoxy.

30

Amino groups may be substituted for example by one or two optionally substituted alkyl, acyl or sulfonyl groups, or two substituents can form a ring, preferably a 5 to 7-membered ring, which may be substituted and may contain other heteroatoms, for example morpholine, thiomorpholine, or piperidine.

35

The term acyl includes the residue of sulfur and phosphorus containing acids as well as carboxylic acids. Examples of acyl groups are thus  $-\text{COR}^5$ ,  $-\text{COOR}^5$ ,  $-\text{CXNR}^5\text{R}^6$ ,  $-\text{CON}(\text{R}^5)\text{OR}^6$ ,  $-\text{COONR}^5\text{R}^6$ ,  $-\text{CON}(\text{R}^5)\text{NR}^6\text{R}^7$ ,  $-\text{COSR}^5$ ,  $-\text{CSSR}^5$ ,  $-\text{S}(\text{O})_p\text{R}^5$ ,  $-\text{S}(\text{O})_2\text{OR}^5$ ,  $-\text{S}(\text{O})_p\text{NR}^5\text{R}^6$ ,  $-\text{P}(=\text{X})(\text{OR}^5)(\text{OR}^6)$ ,  $-\text{CO-COOR}^5$ , where X,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$  are as defined for  $\text{R}^1$ , or  $\text{R}^6$  and  $\text{R}^7$  together with the atom(s) to which they are attached can form a ring, and p is 1 or 2.

In a preferred group of compounds m is 0 and n is 1 or 2.

Most of the compounds of formula I are new, and we therefore provide the novel compounds *per se* and in particular compounds as defined above, where:

Y is hydrogen or methyl;

Z is an oxadiazole, thiadiazole, oxazole, oxazoline, thiazole or thiazoline group, optionally substituted by alkyl, especially methyl, haloalkyl, especially

dichloromethyl, alkoxy, preferably methoxy, alkylthio, preferably methylthio, cyclopropyl or phenyl, optionally substituted, preferably by halo or alkoxy;

X is O;

$\text{R}^2$  is halogen, preferably chloro, alkoxy, preferably methoxy, cyano, or two  $\text{R}^2$  groups together form a methylenedioxy group;

m is 0; and

n is 1 or 2.

The compounds of the invention have activity against a wide range of pathogens of Deuteromycete, Ascomycete, Phycomycete and Basidiomycete origin, and especially against fungal diseases of plants, e.g. mildews and particularly cereal powdery mildew (*Erysiphe graminis*) and vine downy mildew (*Plasmopara viticola*), rice blast (*Pyricularia oryzae*), rice sheath blight (*Pellicularia sasakii*), apple scab (*Venturia inaequalis*) and glume blotch (*Leptosphaeria nodorum*).

The compounds of the invention are generally formulated in conventional compositions used for fungicides. These compositions can contain one or more additional pesticides, for example compounds known to possess herbicidal, fungicidal, insecticidal, acaricidal or nematocidal properties.

The diluent or carrier in the composition of the invention can be a solid or a liquid optionally in association with a surface-active agent, for example a dispersing agent, emulsifying agent or wetting agent. Suitable surface-active agents include anionic compounds such as a carboxylate, for example a metal carboxylate of a long chain fatty acid; an N-acylsarcosinate; mono- or di-esters of phosphoric acid with fatty alcohol ethoxylates or salts of such esters; fatty alcohol sulfates such as sodium dodecyl sulfate, sodium octadecyl sulfate or sodium cetyl sulfate; ethoxylated fatty alcohol sulfates; ethoxylated alkylphenol sulfates; lignin sulfonates; petroleum sulfonates; alkyl-aryl sulfonates such as alkyl-benzene sulfonates or lower alkylnaphthalene sulfonates, e.g. butyl-naphthalene sulfonate; salts of sulfonated naphthalene-formaldehyde condensates; salts of sulfonated phenol-formaldehyde condensates; or more complex sulfonates such as the amide sulfonates, e.g. the sulfonated condensation product of oleic acid and N-methyl taurine or the dialkyl sulfosuccinates, e.g. the sodium sulfonate of dioctyl succinate. Nonionic agents include condensation products of fatty acid esters, fatty alcohols, fatty acid amides or fatty-alkyl- or alkenyl-substituted phenols with ethylene oxide, fatty esters of polyhydric alcohol ethers, e.g. sorbitan fatty acid esters, condensation products of such esters with ethylene oxide, e.g. polyoxyethylene sorbitan fatty acid esters, block copolymers of ethylene oxide and propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, or ethoxylated acetylenic glycols. Examples of a cationic surface-active agent include, for instance, an aliphatic mono-, di-, or polyamine as an acetate, naphthenate or oleate; an oxygen-containing amine such as an amine oxide or polyoxyethylene alkylamine; an amide-linked amine prepared by the condensation of a carboxylic acid with a di- or polyamine; or a quaternary ammonium salt.

The compositions of the invention can take any form known in the art for the formulation of agrochemicals, for example, a solution, a dispersion, an aqueous emulsion, a dusting powder, a seed dressing, a fumigant, a smoke, a dispersible powder, an emulsifiable concentrate or granules. Moreover it can be in a suitable form for direct application or as a concentrate or primary composition which requires dilution with a suitable quantity of water or other diluent before application.

As a dispersion, the composition comprises a compound of the invention dispersed in a liquid medium, preferably water. It is often convenient to supply the consumer with a primary composition which can be diluted with water to form a dispersion having the desired concentration. The primary composition can be provided in any one of the following forms. It can be a dispersible solution which comprises a compound of the invention dissolved in a water-miscible solvent with the addition of a dispersing agent. A further alternative comprises a compound of the invention in the form of a finely ground powder in association with a dispersing agent and intimately mixed with water to give a paste or cream which can if desired be added to an emulsion of oil in water to give a dispersion of active ingredient in an aqueous oil emulsion.

An emulsifiable concentrate comprises a compound of the invention dissolved in a water-immiscible solvent together with an emulsifying agent and which is formed into an emulsion on mixing with water.

A dusting powder comprises a compound of the invention intimately mixed with a solid pulverulent diluent, for example, kaolin.

A granular solid comprises a compound of the invention associated with similar diluents to those which may be employed in dusting powders, but the mixture is granulated by known methods. Alternatively it comprises the active ingredient adsorbed or absorbed on a pre-granular diluent, for example, Fuller's earth, attapulgite or limestone grit.

A wettable powder usually comprises the active ingredient in admixture with a suitable surfactant and an inert powder diluent such as china clay.

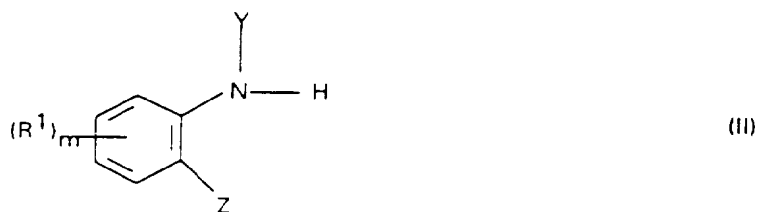
Another suitable concentrate, particularly when the product is a solid, is a flowable suspension concentrate which is formed by grinding the compound with water, a wetting agent and a suspending agent.

The concentration of the active ingredient in the composition of the present invention is preferably within the range of 1 to 30 per cent by weight, especially 5 to 30 per cent by weight. In a primary composition the amount of active

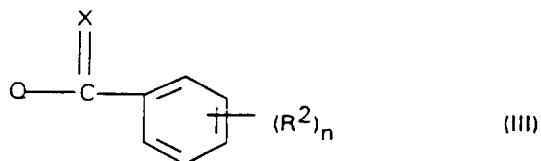
ingredient can vary widely and can be, for example, from 5 to 95 per cent by weight of the composition.

Compounds of formula II may be prepared as described in UK Patent No 1563664  
5 or by analogous processes

The compounds of formula I may in many cases be prepared by reacting a compound of formula II:



10 where Y, Z, R¹ and m are as defined hereinbefore, in the presence of a base, e.g. an organic tertiary amine, with a compound of formula III:



where X, R² and n are as defined hereinbefore and Q is a leaving group, preferably a halogen and especially chlorine, to give the desired compound.

15

The reaction is generally carried out in the presence of a solvent, e.g. an ether.

The compounds of formulae II and III are either known or can be prepared in known manner.

20

Compounds where Y is not hydrogen may be prepared from compounds of formula I where Y is hydrogen, by reaction with a compound of formula Y-Hal, where Y is as defined hereinbefore, and Hal is a halogen, particularly iodine, in the presence of a base.

25



If desired, the compounds produced by the above methods may be modified in known manner to give other compounds of formula I. In particular the compounds of formula I where X is S may be made from the corresponding compounds where X is O by methods analogous to those described for similar conversions in our  
5 WO 95/25723.

Compounds may also be prepared by ring closing in known manner an appropriate starting material to form the heterocyclic groups as will be clear from the

#### Examples

10

The invention is illustrated in the following Examples. Structures of isolated novel compounds were confirmed by NMR and/or other appropriate analyses.

Temperatures are in °C.

#### Example 1

15 3-Cyano-4-methoxybenzoic acid (0.45 g) was heated under reflux in thionyl chloride (15 ml) for about 1 ½ hours, and the solution was then cooled, evaporated under reduced pressure, treated with dry toluene, and evaporated again. It was then dissolved in dry tetrahydrofuran (5 ml) and was added dropwise to 2-(5-methyl-1,3,4-thiadiazol-2-yl)aniline (0.49 g) and triethylamine (0.39 ml) in dry  
20 tetrahydrofuran (10 ml) cooled to 5 °C. The mixture was stirred overnight, after which it was evaporated, then partitioned between water and dichloromethane, with the dichloromethane extract being washed with water three times, then with dilute brine, before being dried over magnesium sulfate. Recrystallisation from ethyl acetate gave 3-cyano-4-methoxy-2'-(5-methyl-1,3,4-thiadiazol-2-yl)-  
25 benzanilide, m.p. 233-5 °C.

#### Example 2

Sodium hydride (0.1 g, 60% dispersion in oil) was added portionwise to a stirred suspension of Compound 14 (see in table below) (0.68 g) in a mixture of dry  
30 tetrahydrofuran (20 ml) and dimethylformamide (2 ml) at room temperature under nitrogen. The mixture was stirred for 30 minutes and methyl iodide (0.15 ml) added. The mixture was stirred at room temperature overnight, then quenched by the dropwise addition of methanol in tetrahydrofuran followed by water. The tetrahydrofuran was evaporated under reduced pressure and the residue was  
35 partitioned between ethyl acetate and water. The aqueous layer was extracted

with ethyl acetate and the combined ethyl acetate extracts were washed with brine, dried and evaporated under reduced pressure. The residue was purified by silica gel column chromatography followed by trituration with diisopropyl ether to give N-methyl-3,4-methylenedioxy-2'-(5-methyl-1,3,4-thiadiazol-2-yl)benzanilide, m.p. 126.5-8°C.

### Example 3

A solution of 3,4-dimethoxybenzoyl chloride (2 g) in dry tetrahydrofuran (20 ml) was added dropwise to a cooled, stirred solution of anthranilamide oxime (0.76 g) in dry tetrahydrofuran (35 ml) and triethylamine (1.01 g). The mixture was stirred at room temperature overnight, evaporated under reduced pressure and the residue partitioned between dichloromethane and water. The aqueous layer was extracted with dichloromethane and the combined organic extracts washed with brine, dried and evaporated under reduced pressure. The residue was recrystallised from ethyl acetate to give 2'-[amino(3,4-dimethoxybenzoyloxyimino)-methyl]-3,4-dimethoxybenzanilide, m.p. 183-3.5°C.

A stirred suspension of this compound (0.48 g) in acetone (20 ml) was treated with 5% aqueous sodium carbonate (3.6 ml) and the mixture stirred at room temperature for 2 days. It was filtered and the solid was washed with small amounts of acetone and dried in air. The filtrate was concentrated under reduced pressure and a solid collected and combined with the other solid to give 2'-[(5-(3,4-dimethoxyphenyl)-1,2,4-oxadiazol-3-yl)-3,4-dimethoxybenzanilide, m.p. 230°C.

### Example 4

A mixture of Compound 7 (see in table below) (0.87 g) and Lawesson's reagent in dry tetrahydrofuran (50 ml) was heated under reflux for 19 hours. The mixture was poured into brine and extracted with ether and the extract dried with magnesium sulphate and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to give 3,4-dimethoxy-2'-(5-methyl-1,2,4-oxadiazol-3-yl)-thiobenzanilide, m.p. 126-7°C.

Example 5

A mixture of 3,4-methylenedioxybenzoic acid (0.83 g) and thionyl chloride (50 ml) was heated under reflux for one hour. The mixture was cooled to room temperature and excess thionyl chloride removed under reduced pressure. The residue was dissolved in tetrahydrofuran, stirred and cooled to below 10°C. A solution of 2-[3-(4-chlorophenyl)-1,2,4-oxadiazol-5-yl]aniline (1.4 g) and triethylamine (1 ml) in tetrahydrofuran (100 ml) was added. The mixture was stirred at room temperature overnight then water (500 ml) was added and the organic layer separated and dried over magnesium sulphate. The solvent was removed under reduced pressure and the residue purified by silica gel column chromatography to give 2'-[3-(4-chlorophenyl)-1,2,4-oxadiazol-5-yl]-3,4-methylenedioxybenzanilide, m.p. 155-7°C.

The starting material was prepared by stirring together for half an hour 4-chlorobenzamidoxime (17 g) with a suspension of dry potassium carbonate (7 g) in dioxane (300 ml). A mixture of isatoic anhydride (16.3 g) in dioxane (50 ml) was then added and the mixture stirred at room temperature overnight. Solvent was removed under reduced pressure and the residue dissolved in acetic acid to give a volume of 500 ml and heated under reflux for 4 hours. Solvent was removed under reduced pressure and the residue diluted with water and extracted with ethyl acetate. The extracts were washed with water, dried and evaporated under reduced pressure. The residue was purified by crystallisation from light petroleum (b.p. 80-100°C) followed by crystallisation with cyclohexane to give the desired product, m.p. 142-4°C.

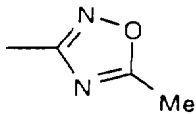
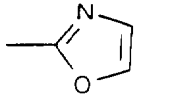
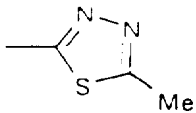
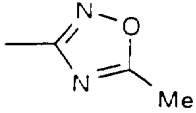
Example 6

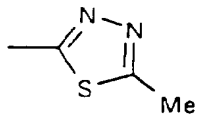
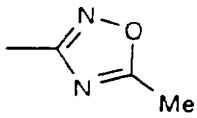
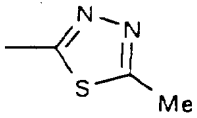
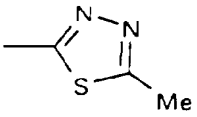
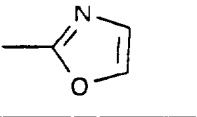
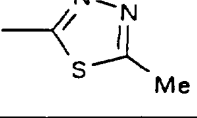
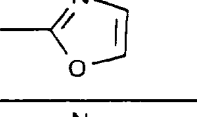
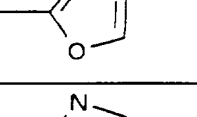
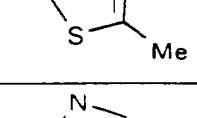
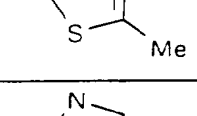
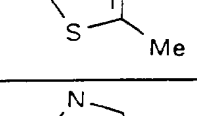
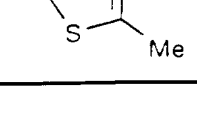
Phosphoryl chloride (5.2 g) was added to a stirred suspension of 3,4-methylenedioxybenzoic acid (4.98 g) in dry toluene (60 ml). The mixture was stirred at room temperature overnight and then cooled to 0-5°C. A solution of anthranilonitrile (3.54 g) and triethylamine (9.11 g) in dry tetrahydrofuran (60 ml) was added dropwise and the mixture stirred and allowed slowly to reach room temperature. It was left to stand over the weekend, diluted with water and dichloromethane and the aqueous layer extracted with dichloromethane. The combined organic extracts were washed with aqueous sodium hydrogen carbonate and brine, dried and evaporated under reduced pressure. The residue was

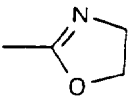
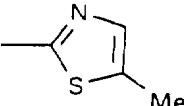
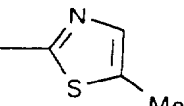
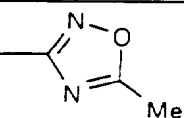
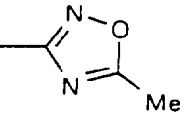
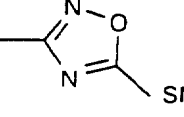
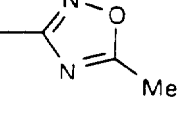
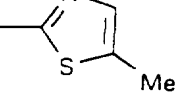
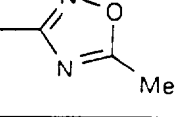
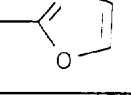
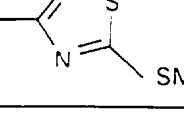
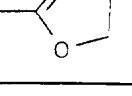
trituated with diethyl ether and the residue purified by silica gel column chromatography to give 2-cyano-3,4-methylenedioxybenzanilide. This compound (1.18 g) was added as a slurry in ethanol (40 ml) to a stirred solution of potassium carbonate (0.61 g) and hydroxylamine hydrochloride (0.62 g) in water (15 ml) at room temperature. The mixture was stirred for 10 minutes and then heated slowly to reflux and maintained at reflux for 3 hours. The mixture was cooled and left to stand overnight. The precipitate was collected by filtration, washed and dried to give 2'-[amino(hydroxyimino)methyl]-(3,4-methylenedioxybenzanilide, m.p. 187-8°C.

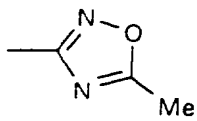
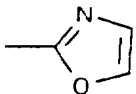
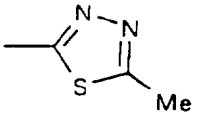
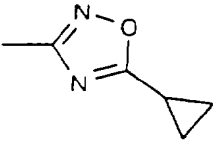
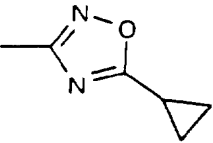
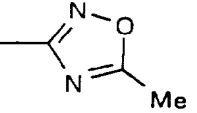
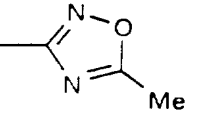
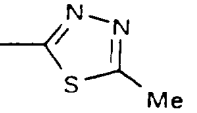
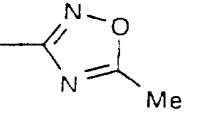
A mixture of this compound (1 g) and dichloroacetic anhydride (1.6 g) in glacial acetic acid (80 ml) was heated under reflux for one hour. The mixture was allowed to cool and then evaporated under reduced pressure. The residue was added to water and extracted with ethyl acetate. The extracts were washed with water and dried and evaporated under reduced pressure. The residue was recrystallised from light petroleum (b.p. 80-100°C) to give 2'-(5-dichloromethyl-1,2,4-oxadiazol-3-yl)-3,4-methylenedioxybenzanilide, m.p. 125-9°C

The following compounds of formula I where X is O, were prepared by methods analogous to that described in the previous Examples:

Ex	(R <sup>2</sup> ) <sub>n</sub>	Y	(R <sup>1</sup> ) <sub>m</sub>	Z	m.p.(°C)
7	3,4-(OMe) <sub>2</sub>	H	-		138-40
8	3,4-(OMe) <sub>2</sub>	H	-		164-5
9	3-Cl	H	-		188-90
10	3,4-(OMe) <sub>2</sub>	Me	-		115-6

Ex	(R <sup>2</sup> ) <sub>n</sub>	Y	(R <sup>1</sup> ) <sub>m</sub>	Z	m.p.(°C)
11	3,4-(OMe) <sub>2</sub>	H	-		176-7
12	3,4-OCH <sub>2</sub> O-	H	-		155-6
13	-	H	-		148-9
14	3,4-OCH <sub>2</sub> O-	H	-		200-1
15	-	H	-		149-51
16	3-Cl	Me	-		syrup
17	3-Cl	H	-		161-2
18	3,4-OCH <sub>2</sub> O-	H	-		163-4
19	3-Cl	H	-		119-21
20	-	H	-		107-9
21	3,4-OCH <sub>2</sub> O-	H	-		168-9.5
22	2-CF <sub>3</sub>	H	-		128-9.5

Ex	(R <sup>2</sup> ) <sub>n</sub>	Y	(R <sup>1</sup> ) <sub>m</sub>	Z	m.p.(°C)
23	3,4-(OMe) <sub>2</sub>	H	-		165-7
24	2-Me	H	-		115-6
25	3,4,5-(OMe) <sub>3</sub>	H	-		158-9
26	3-Cl,4-OMe	Me	-		192-3
27	2-CF <sub>3</sub>	H	-		149-50.5
28	3,4-OCH <sub>2</sub> O-	H	-		62-5
29	3-Br,4-OMe	H	-		214.5-5
30	3-Br,4-OMe	H	-		205-6
31	3-Br	H	-		127-9
32	4-I	H	-		179-80.5
33	3,4-OCH <sub>2</sub> O-	H	-		154-6
34	2-F	H	-		128-30.5

Ex	(R <sup>2</sup> ) <sub>n</sub>	Y	(R <sup>1</sup> ) <sub>m</sub>	Z	m.p.(°C)
35	4-OMe	H	4,5-(OMe) <sub>2</sub>		158-9
36	4-CF <sub>3</sub> O	H	-		116-7
37	4-OMe	H	6-Me		137.5-9.5
38	2-CF <sub>3</sub>	H	-		148.5-9.5
39	3,4-OCH <sub>2</sub> O-	H	-		149.-50.5
40	3,4-OCH <sub>2</sub> O-	Me	-		syrup
41	4-Ph	H	-		134-5.5
42	-	COMe	-		syrup
43	2-OMe,4-SMe	H	-		137-8

### Test Example

Compounds are assessed for activity against one or more of the following:

*Plasmopara viticola*: vine downy mildew

*Erysiphe graminis f. sp. hordei*: barley powdery mildew

*Erysiphe graminis f. sp. tritici*: wheat powdery mildew

*Pyricularia oryzae*: rice blast

*Pellicularia sasakii*: rice sheath blight

*Leptosphaeria nodorum*: glume blotch

Aqueous solutions or dispersions of the compounds at the desired concentration,  
5 including a wetting agent, were applied by spray or by drenching the stem base of  
the test plants, as appropriate. Plants or plant parts were then inoculated with  
appropriate test pathogens and kept under controlled environment conditions  
suitable for maintaining plant growth and development of the disease. After an  
appropriate time, the degree of infection of the affected part of the plant was  
10 visually estimated. Compounds were considered active if they gave greater than  
50% control of the disease at a concentration of 500 ppm (w/v) or less.

Compounds 4, 7, 13, 24, 25, 28, and 31 showed activity against *Plasmopara*  
*viticola*;

15 Compound 1 showed activity against *Erysiphe graminis f. sp. hordei*;

Compounds 9, 17 and 18 showed activity against *Pyricularia oryzae*;

Compound 27 showed activity against *Pellicularia sasakii*;

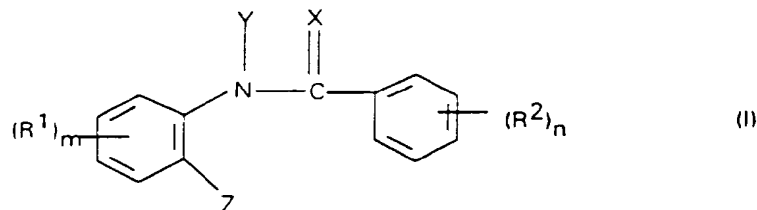
Compounds 4, 15, 16, 31 and 34 showed activity against *Leptosphaeria nodorum*;  
and

20 Compounds 1-4, 6, 7, 8, 11-14, 18, 19, 21, 23-27, 29-31, 33, 39 and 40  
showed activity against *Erysiphe graminis f. sp. tritici*



## CLAIMS

1. The use as fungicides of the compounds of formula I:



5 where:

each R<sup>1</sup> and each R<sup>2</sup> is an optionally substituted alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl or amino group, the group Y-X-, halogen, cyano, nitro, acyl, heterocyclyl, heterocyclyloxy, aryl or aryloxy; or two adjacent groups together with the carbon atoms to which they are attached form an optionally substituted ring;

Y is hydrogen, acyl, or an optionally substituted alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl group;

Z is an optionally substituted 5 membered heterocyclic group comprising 2 or 3 ring heteroatoms selected from nitrogen, oxygen and sulfur, the group being attached to the phenyl through a carbon atom;

X is O or S;

m is 0 to 4; and

n is 0 to 5.

2. The compounds of formula I as defined in claim 1 where:

Y is hydrogen or methyl;

Z is an oxadiazole, thiadiazole, oxazole, oxazoline, thiazole or thiazoline group, optionally substituted by alkyl, haloalkyl, alkoxy, alkylthio, cyclopropyl or optionally substituted phenyl;

X is O;

R<sup>2</sup> is halogen, preferably chloro, alkoxy, preferably methoxy, cyano, or two R<sup>2</sup> groups together form a methylenedioxy group;

m is 0; and

n is 1 or 2.

3. Fungicidal compositions which comprise a compound as defined in claim 1 or 2 in admixture with an agriculturally acceptable diluent or carrier.
4. A method of combating phytopathogenic fungi at a locus infested or liable
- 5 to be infested therewith, which comprises applying to the locus a compound as defined in claim 1 or 2.

# INTERNATIONAL SEARCH REPORT

Int. onal Application No  
PCT/GB 96/02279

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D285/12 C07D417/12 C07D271/06 C07D413/12 C07D263/32  
C07D277/28 C07D263/10 A01N43/82 A01N43/76 A01N43/78

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 1 563 664 A (SUMITOMO CHEMICAL CO) 26 March 1980 see page 1, line 22 - page 2, line 15; claims; examples	1-4
P,Y	--- WO 95 25723 A (AGREVO UK LTD ;RIORDAN PETER DOMINIC (GB); BODDY IAN KENNETH (NZ);) 28 September 1995 cited in the application see examples, e.g. 114, 123, 177 see page 5, line 8 - line 25; claims --- -/--	1-4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

13 December 1996

Date of mailing of the international search report

20.12.1996

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# INTERNATIONAL SEARCH REPORT

Int. onal Application No  
PCT/GB 96/02279

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>CHEMICAL ABSTRACTS, vol. 125, no. 7, 12 August 1996 Columbus, Ohio, US; abstract no. 86664, YOSHIKAWA, YUKIHIRO ET AL.: "Preparation of N-acyl-2-heterocyclylaniline derivatives as agricultural and horticultural fungicides" XP002020962 see abstract &amp; JP 08 092 223 A (MITSUI TOATSU CHEMICALS) 9 April 1996 -----</p>	1-4

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/02279

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-C- 1082566	29-01-82
		JP-A- 53099324	30-08-78
		JP-B- 56022841	27-05-81
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		JP-A- 53113022	03-10-78
		JP-B- 56022842	27-05-81
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		CA-A- 1111051	20-10-81
		FR-A- 2392961	29-12-78
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WO-A-9525723	28-09-95	AU-A- 1898195	09-10-95
		ZA-A- 9502205	31-10-95
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